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BENTONITE SUBSTITUTES - A PROGRESS REPORT

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by

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ABSTRACT

Various combinations of Na, Ca and NH_4 lignosulphonates with Na and Ca bentonites were tested as binders in making iron ore pellets. Lignosulphonates alone were substandard but certain mixtures of Na bentonite with Na and NH_4 lignosulphonates gave adequate results.

SUBSTITUTS DE BENTONITE - RAPPORT SUR L'ÉTAT D'AVANCEMENT DES TRAVAUX

par

J. Wilson

RÉSUMÉ

On a fait l'essai de plusieurs combinaisons de lignosulfonates Na, Ca et NH_4 avec des bentonites Na et Ca en tant que liants dans la fabrication de boulettes de minerai de fer. Les résultats ont montré que les lignosulfonates utilisés seuls étaient médiocres, mais que certains mélanges de bentonite Na avec des lignosulfonates Na et NH_4 ont donné des résultats satisfaisants.

INTRODUCTION

CANMET is presently involved in developing a substitute for bentonite used as a binder in iron ore pelletizing. The Canadian iron ore industry is becoming less competitive due to the development of new high-grade iron ore deposits around the world whose upgrading costs are minimal. In order to maintain Canada's place as an iron ore exporter we must develop new technologies which will enable us to compete in the world market. One possible area for improvement is the development of a substitute for bentonite. Bentonite as a binder in iron ore is expensive, variable in quality, must be imported, degrades the concentrate and contains harmful alkalis. As well, it is suspected that the presence of fine-grained silica in the blast furnace burden adversely affects reducibility. To meet these demands it is obvious that a candidate substitute should be cheaper than bentonite, be of uniform composition, be available in Canada, or even better, be locally available to the pelletizing plant, be organic or be a volatile inorganic and contain little or no silica or alkali's.

The search for a substitute has continued more or less for thirty years and it appears to have reached the stage where any new candidate will likely have to be either an upgraded or manufactured commodity. Such a substance must therefore be made from very cheap raw materials to meet the criterion of being at least as economical as bentonite. Cheap raw materials would include industrial waste products and local low-grade clays.

POSSIBLE BENTONITE SUBSTITUTES

The following is a list of possible substitutes:

Lignosulphonates and clays
Montmorillonite-bearing clays
Whey
Sawdust
Red mud from the aluminum industry
Seaweed extract

All of the substances in this list have been tried before and are mentioned in the literature. However they were not developed to any great extent and should be thoroughly investigated.

Lignosulphonates alone do not make good binders. However they are known to have excellent dry strengths when used with ceramic-type clays. Therefore it is possible that lignosols and cheap local clays mixed together could form a suitable binder in pelletizing.

According to reports by Brady and Dean (1,2) there are some clay deposits in Canada which contain appreciable quantities of montmorillonoid-type minerals. It is therefore possible to upgrade such clays by mineral benefication techniques and cationic activation. Presently the USBM is working on the upgrading of local clays near the Mesaba Range in Minnesota by activation with various additives (3).

Whey, which is a waste byproduct of the dairy industry, has been tried successfully with other additives to bind iron ore briquettes before curing (4). This binder has never been tried in pelletizing, according to the literature.

Sawdust was successfully used as an additive in Japan to improve reducibility of the fired pellets but was rejected on cost alone. Its effect on green ball formation was not published but it is known to absorb water readily. Canada has a plentiful supply of inexpensive sawdust.

Red mud is a byproduct of the aluminum industry and is available from ALCAN at Arvida, Quebec. It assays 23% SiO_2 and 18% Fe_2O_3. It has already been investigated at CANMET (5) and was found to be inferior. However it was never tried in conjunction with other binders.

Seaweed extract, alginate, was successfully tried at IOC but was expensive to use at that time (6). It was suggested by Major-Marothy that a cheaper alginate could be made if it was less highly refined. Seaweed is locally available to the Quebec-Labrador producers so that transportation costs would be much less than for bentonite.

Investigations of the candidate binders listed above outline the work planned by the author in the search for a substitute for bentonite. The rest of the report contains the work done to date on the first option - lignosulphonates and clays.

LIGNOSULPHONATE - CLAY MIXTURES

The active ingredient in bentonite is Na-montmorillonite. Na-montmorillonite has the ability to absorb and immobilize water which is the most important property of bentonite as a binder. However worldwide, Ca-bentonite is much more abundant. Ca-bentonite, which contains Ca-montmorillonite does absorb water to a certain extent but not as readily as the Na-type. Ca-bentonite is used as a binder in the ceramic industry where it is known to produce high dry strengths in ceramic clay bodies. Lignosulphonates are also used as a binder in the clay industry. It has been suggested (7) that a calcium-based lignosulphonate would form a good dry bond with a clay not saturated with respect to calcium ions. This suggests further that it may be possible to utilize non-Na-montmorillonite bentonites or other low grade clays mixed with a suitable lignosulphonate to produce a binder which will be cheaper than imported bentonite and contribute less silica.

EXPERIMENTAL

The iron ore concentrate used for the balling experiments came from Sidbec-Normines pelletizing plant at Port Cartier. The material was air dried for several weeks and then split into 2800 g allotments. The moisture content was bone dry and the size distribution is given in Table 1.

Table 1. Size distribution of balling feed from Sidbec-Normines

Sieve Size (μm)	Sieve Size (Mesh)	Wt Retained (%)	Cumulative Wt Passing (%)
75	200	10.6	89.4
45	325	19.3	70.1
38	400	8.5	61.6
-38	-400	61.6	-

Three bentonites were chosen for study in the initial series of tests. These were Avonlea - a non-activated Na-bentonite from Saskatchewan, Pembina - a Ca-bentonite from Manitoba, and a western bentonite supplied by Sidbec-Normines. A high quality Wyoming bentonite was also tried for comparison. Three of these were assayed and tested for absorption. The results are found in Tables 2 and 3.

Table 2. Chemical composition of bentonites

Bentonite	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	S	CO_2	LOI
Avonlea	57.56	16.49	4.23	1.80	2.40	2.09	0.29	0.24	0.84	14.70
Pembina	51.72	16.97	3.76	1.34	3.16	0.36	0.66	0.54	1.08	21.62
Wyoming	56.75	20.28	4.10	1.28	2.60	2.10	0.12	0.18	1.36	5.60

Table 3. Water absorption tests

Bentonite	Wt % Increase
Avonlea	545
Pembina	166
Wyoming	1046

Three lignosulphonates were chosen with various cations Ca^{2+}, Na^{+}, and NH_4^{+} to study the effect of any interaction with the clays. The batch ball method was used to form the balls. The dry 2800 g sample was added to a Hobart mixer, 227 g of distilled H_2O were added and the charge was mixed for five minutes. Then the dry binder was added and the charge was mixed

for an additional five minutes. Seventy grams of -4.75 + 3.35 mm (-4 + 6 mesh) seeds were next prepared by balling in the airplane tire and screening the product. It was found that the weight of seeds was important in forming a sufficient number of correctly sized balls in the next step. The seeds are then put back into the tire, wetted and then the rest of the charged was sprinkled slowly over the seeds during a three minute period, faster as the balls grew. Distilled water was added as a spray to aid ball growth during this time. The balls are then rolled for an additional minute to form them and are then screened at -12.5 + 11.2 mm (-1/2" + 14/32"). The balls were then measured for drop strength, wet strength and dried for moisture content and dry strength. Twenty balls were used for each test and the results averaged. The variables for this experiment were three lignosulphonates, three bentonites, and four binder mixes. Moisture content and mixing time were constant. Repeats were done on selected tests.

RESULTS

The minimum pellet qualities generally accepted by the industry for pellets made in the plant are a drop number of five, a wet strength of 9 N and a dry strength of 44 N. The results of all the tests to date are listed in Table 4 and some averaged results are plotted in Fig. 1 to 3. The results show the following.

1. There is a maximum in the drop strength and wet strength for Sidbec bentonite at a dosage rate of .47% which does not appear for the other two bentonites.

2. Lignosulphonate has no affect on the Avonlea and Pembina drop test but Na-lignosulphonate reduces drop strength in Sidbec bentonite.

3. Lignosulphonate reduces wet strength. In fact, using lignosulphonate alone is worse than no additive at all with respect to wet strength.

4. The lignosulphonates tested generally maintained the dry strength at an acceptable level. When used with the Ca-bentonite (Pembina) the lignosulphonates raised the dry strength to an acceptable level.

Table 4. Experimental results

Binder mix				H2O (%)	Drop No.	Wet Strength (N)	Dry Strength (N)
Bentonite Type	(Wt % Dry)	Lignosulphonate Type	(Wt % Dry)				
Wyoming	0.7	Nil	-	8.3	5.7	11.4	89
*Wyoming	0.7	Nil	-	8.2	8.0	11.8	89
Sidbec	0.7	Nil	-	8.0	3.4	9.5	85
*Sidbec	0.7	Nil	-	7.6	4.1	11.0	85
Nil	-	Nil	-	6.1	2	7.5	3
Nil	-	Ca	0.7	-	2	3	-
Nil	-	Na	0.7	6.0	1	4.3	67
Nil	-	NH_4	0.7	6.9	2.2	5.1	65
Avonlea	0.7	Nil	-	7.6	3.9	12.2	112
Pembina	0.7	Nil	-	7.0	3.3	11.1	39
Avonlea	0.23	Ca	0.47	6.3	2.1	6.7	77
Avonlea	0.47	Ca	0.23	7.0	2.8	9.4	98
Avonlea	0.23	Na	0.47	7.0	1.4	5.7	102
Avonlea	0.47	Na	0.23	7.5	3.2	10.2	118
Avonlea	0.47	NH_4	0.23	7.2	3.4	11.3	106
Avonlea	0.23	NH_4	0.47	6.6	1.6	5.5	76
Pembina	0.23	Ca	0.47	6.8	1.8	5.4	76
Pembina	0.47	Ca	0.23	7.2	2.6	7.6	73
Pembina	0.23	Na	0.47	7.6	2.3	5.4	89
Pembina	0.47	Na	0.23	6.7	1.9	7.0	95
Pembina	0.23	NH_4	0.47	7.2	1.5	4.6	73
Pembina	0.47	NH_4	0.23	7.2	2.5	8.5	83
*Sidbec	0.70	Nil	-	7.4	2.8	9.4	70
Sidbec	0.70	Nil	-	7.3	2.8	9.1	68
Sidbec	0.47	Nil	-	7.6	4.4	12.7	58
*Sidbec	0.47	Nil	-	7.3	3.6	12.5	57
Sidbec	0.23	Nil	-	7.1	2.9	11.4	24
*Sidbec	0.23	Nil	-	6.5	2.3	11.9	28
Avonlea	0.47	Nil	-	6.6	2.9	12.3	64
Avonlea	0.23	Nil	-	6.8	2.1	8.8	25
Pembina	0.47	Nil	-	6.6	2.3	9.2	22
Pembina	0.23	Nil	-	6.8	2.0	7.3	11
*Nil	-	Nil	-	7.0	2.2	8.2	2
Sidbec	0.23	Na	0.47	6.6	2.2	8.2	94
*Sidbec	0.23	Na	0.47	6.6	2.4	8.4	103
Sidbec	0.47	Na	0.23	7.2	3.6	12.0	91
*Sidbec	0.47	Na	0.23	6.8	3.0	11.7	89

*Repeats

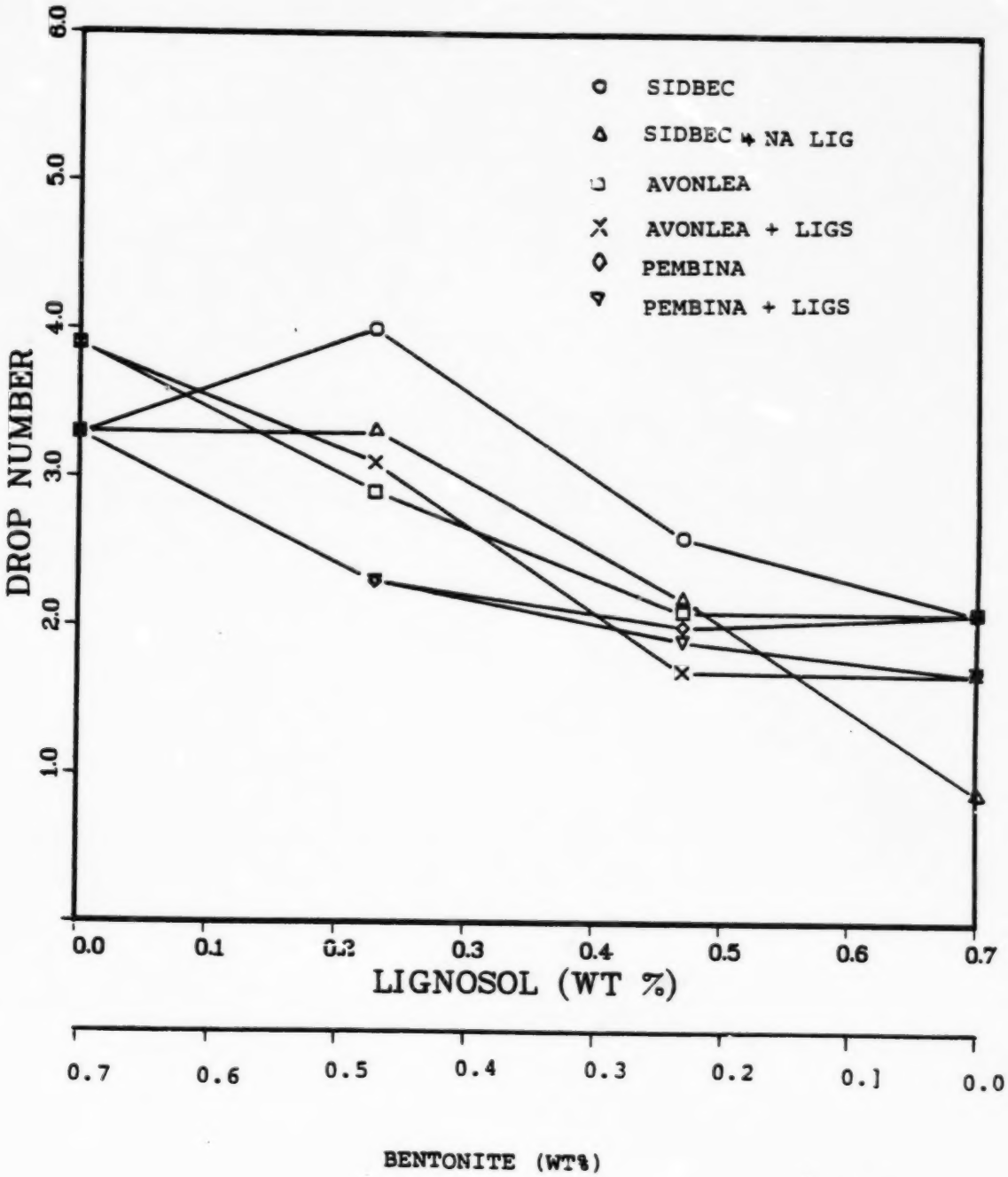

Fig. 1. Drop number vs binder dosage

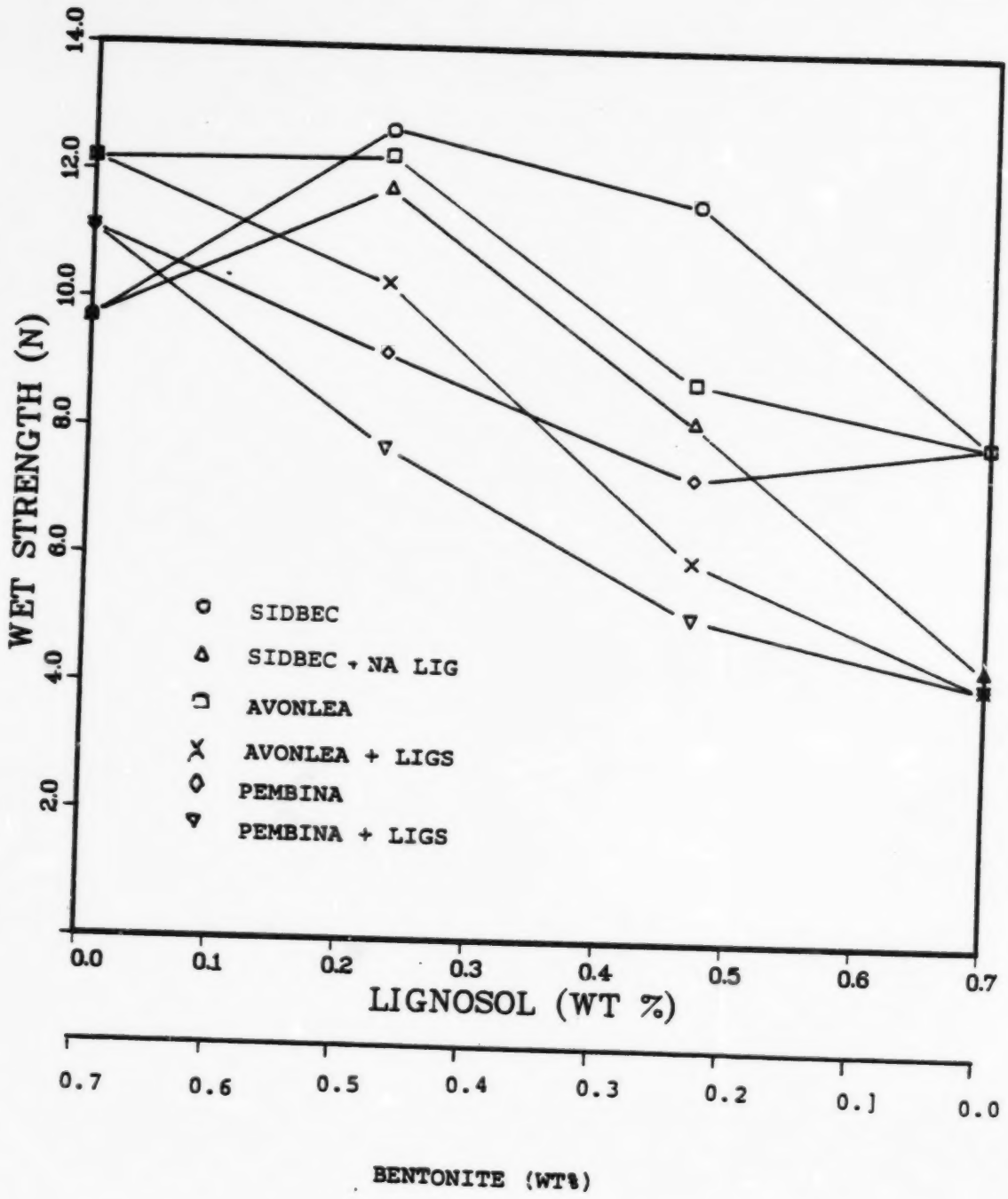

Fig. 2. Wet strength vs binder dosage

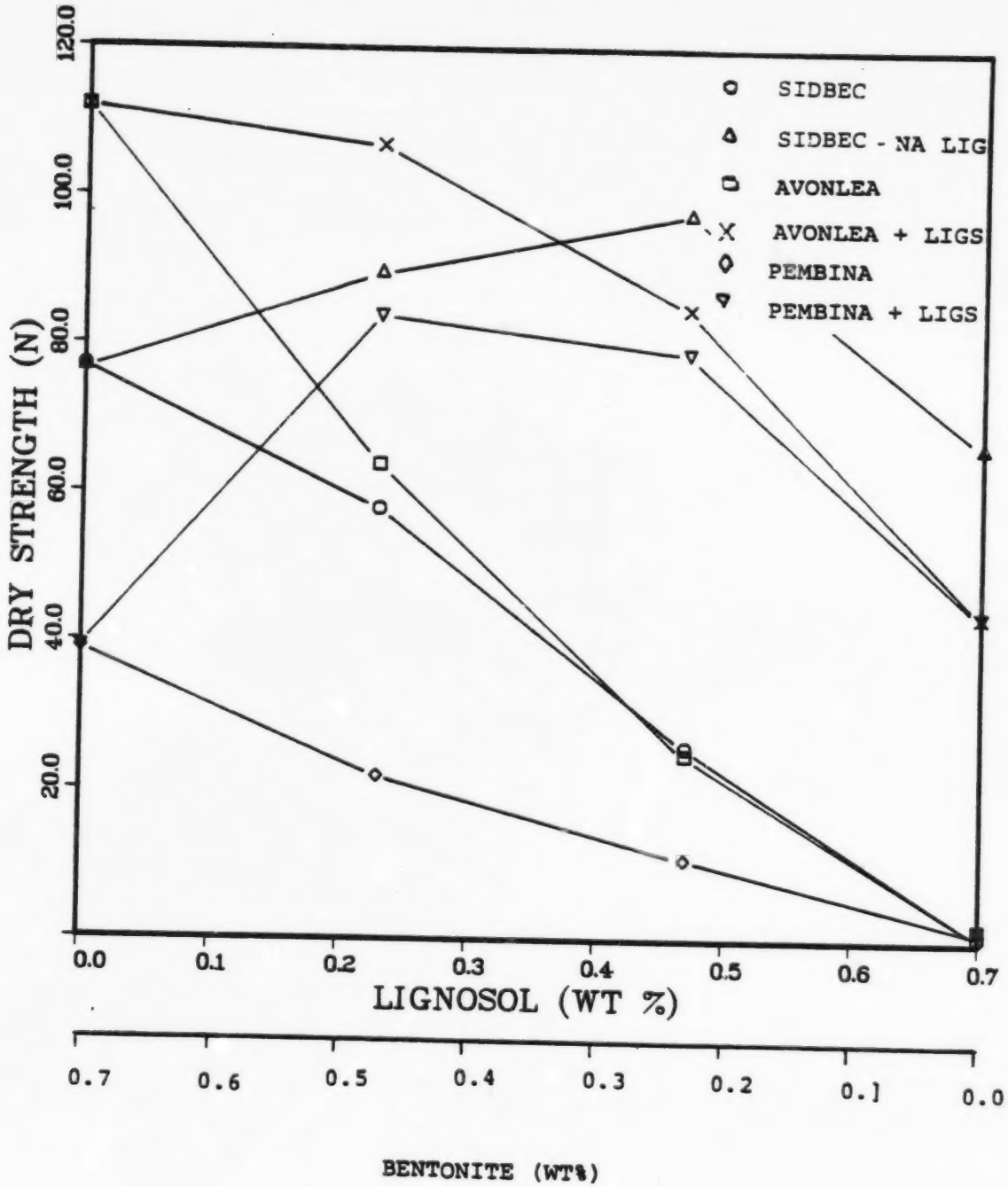

Fig. 3. Dry strength vs binder dosage

5. Green balls made with lignosulphonate/bentonite grew faster, looked shinier, and absorbed less H_2O than balls made with bentonite only. Tests using the lignosulphonate/bentonite binder showed some caking during mixing. This effect increased as the lignosulphonate portion increased.

CONCLUSIONS

The trends of the graphs in Fig. 1 to 3 show that in general lignosulphonate contributes nothing to drop strength, actually decreases wet strength but maintains dry strength at an acceptable level. When used in combination with Sidbec and Pembina bentonites, the dry strength actually improved. Lignosulphonate has poorer ballability than bentonite and this is probably due to its poor control over water mobility.

Thus it is obvious lignosulphonates will never substitute for bentonite alone but will require other additives to give adequate drop and wet strengths. As a partial replacement of bentonite the tests show the following combinations in Table 5 are as good as the standard bentonite.

Table 5. A comparison of the best binder combinations with a standard industrial bentonite

	Drop No.	Wet Strength (N)	Dry Strength (N)
Sidbec Standard (0.7%)	3.3	9.7	77
Sidbec (.47%) Na-lig (.23%)	3.6	11.8	90
Avonlea (.47%) Na-lig (.23%)	3.2	10.2	118
Avonlea (.47%) NH_4-lig (.23%)	3.4	11.3	106

It is interesting to note that Avonlea bentonite outperformed the Sidbec bentonite at the 0.7 wt % dosage rate, keeping in mind that no repeat of the Avonlea test was performed. Also all the tests showed a drop number which was substandard (less than 5) except for the high grade Wyoming bentonite.

Future tests are planned to try to improve drop numbers and wet strengths of lignosulphonate by using C.M.C., lime, slaked lime and dolomite additions. Other local clay types will be tried as well. The effect of mixing times on caking should be examined.

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